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**STRUCTURAL PROPERTIES OF AMORPHOUS
SEMICONDUCTORS BY MOSSBAUER SPECTRO-
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Norman Blum

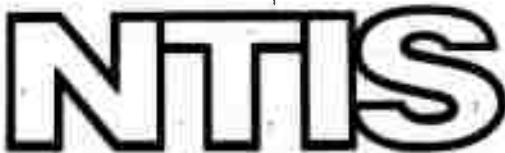
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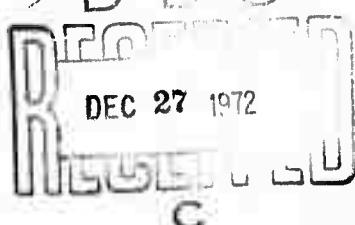
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A. SUMMARY

The Mossbauer technique provides a means for investigating short-range order and order-disorder transitions which are difficult to examine by other techniques. By correlating structural information with sample preparation variables and optical and electronic properties, a significant contribution to understanding the behavior and properties of amorphous semiconductors may be made. Current emphasis is being placed on observing the amorphous to crystalline transition in vacuum deposited Te films.

Since crystallization occurs below room temperature ($\sim 0^\circ\text{C}$) ⁽¹⁾, apparatus was constructed to deposit, transfer and examine films maintained at low temperature. Crystalline films of tellurium up to 18 microns thick have been deposited on room temperature beryllium substrates and Mossbauer spectra have been obtained. The spectra were obtained using an ^{125}I in Cu source since difficulty was experienced in obtaining an originally sought ^{125}Te in $\beta\text{-TeO}_3$ source. Samples enriched with 25% ^{125}Te are now being prepared in order to conduct the low temperature measurements efficiently.

B. MOSSBAUER EFFECT IN TELLURIUM

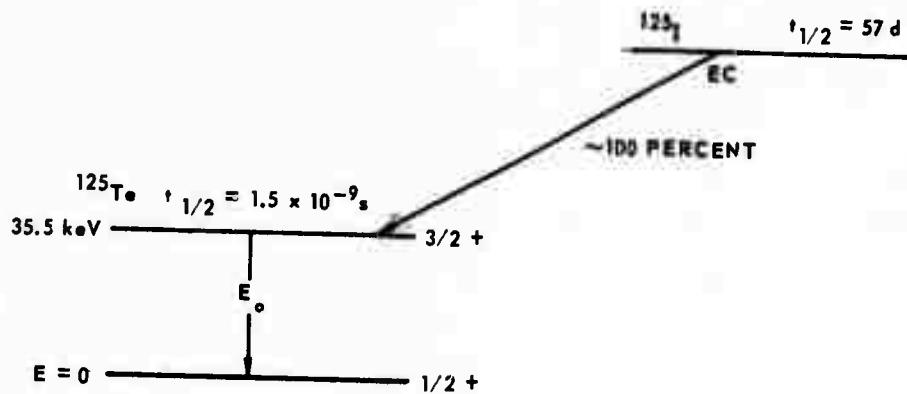
Of all the elements which may be prepared in both amorphous and crystalline forms by vapor deposition, tellurium is the only one which exhibits an appreciable Mossbauer effect for one of its isotopes, ^{125}Te , having a natural abundance of about 7%.

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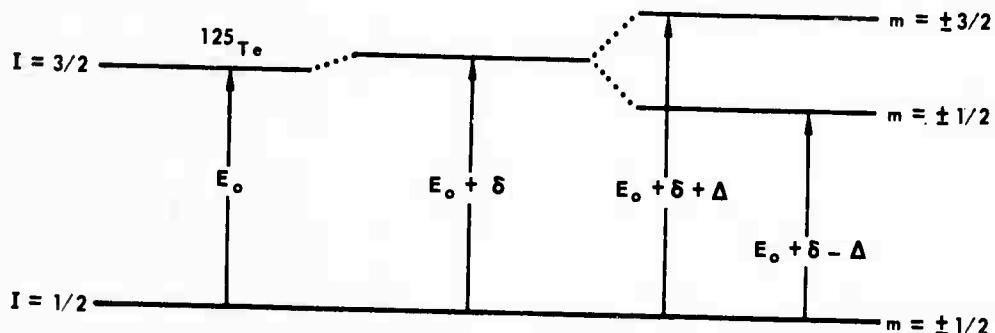
Mossbauer absorption experiments are in many ways analogous to optical absorption experiments in which the gamma ray, emitted and absorbed by the atomic nucleus in a particular isotope, plays the role of the optical photon. By using the gamma ray emitted in the decay of ^{125}I to the 35.5 keV nuclear excited state in ^{125}Te , one may observe the hyperfine interactions between the nuclear multipole moments and the electromagnetic field produced by the atomic electronic charge distributions in stable ^{125}Te (2). Of particular interest in the present investigation are the electric monopole and quadrupole interactions. Figure 1 shows the decay scheme of ^{125}I along with the level scheme of the hyperfine interactions. The s-electron charge density at the ^{125}Te nucleus interacts with the nuclear charge density (monopole term) to produce an energy shift between the ground and excited nuclear states called the isomer shift. There is also a centroid shift due to the second-order Doppler effect (thermal red shift) which is temperature dependent and easily separable from the isomer shift (I.S.); the two effects together are called the chemical or centroid shift (C.S.). Observations of the I.S. for samples of different conductivity under various conditions yield information concerning the conduction mechanism in the samples and the role of the tellurium ions in the conduction process.

The quadrupole interaction between the electric quadrupole moment of the nucleus in the $I = 3/2$, 35.5 keV excited nuclear

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DECAY SCHEME OF ^{125}I SHOWING ORIGIN OF MÖSSBAUER GAMMA RAY OF ENERGY E_0



LEVEL DIAGRAM SHOWING THE ISOMER SHIFT, δ , AND THE QUADRUPOLE SPLITTING, 2Δ , HYPERFINE STRUCTURE
THE MAGNETIC DIPOLE SPLITTING IS NOT SHOWN

Figure 1

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state and the electric field gradient set up by the asymmetry of the surrounding ionic charges yields important and unique information concerning the microscopic structure of the system. The symmetry of the ^{125}Te site is determined from an analysis of the quadrupole splittings and their temperature dependence. This determination in turn provides the key by which we may ascertain the crystalline or amorphous character of the samples. The isomer shifts are anticipated to be of the order 0.1 to 0.5 mm/sec, while the quadrupole splittings for non-cubic symmetry are about 5 mm/sec. Since the line width is about 6 mm/sec, computer aided analysis of the data is essential. Magnetic hyperfine interactions may be induced by subjecting the samples to an external magnetic field. While we are not specifically interested in the magnetic interactions in this case, the overall hyperfine spectrum is often simplified by the application of such an external field, and previously unresolved hyperfine structure thereby made resolvable.

The Mossbauer technique thus provides information concerning the degree of short-range order and coordination symmetry of the atomic site, as well as a quantitative indication of the approach to crystallinity of a sample as a function of its preparation parameters such as temperature, pressure and composition. This characterization, coupled with the knowledge of carefully controlled sample preparation parameters and correlated with detailed experimental and theoretical investigations of the

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electronic and optical properties, should provide useful information as well as valuable insight into understanding and exploiting the properties of amorphous semiconductors.

C. TECHNICAL PROGRESS

a) Spectrometer Calibration and Spectrum Analysis

The Mossbauer spectrometer, including the superconducting magnet, was modified for use with ^{125}Te , placed into operation, and calibrated. Using a 50 mCi ^{125}I in Cu source, spectra have been obtained for suitably prepared samples of TeO_3 , ZnTe and metallic Te. The ZnTe single line absorber gives an indication of the line width and resolution of the system for both source and absorber. With both source and absorber at 80°K, the line width as fit by computer was 7.6 mm/sec, and the maximum absorption was 2.3%. This compares favorably with what has been reported previously for this source/absorber combination.

Spectra of ZnTe, TeO_3 and several specimens of Te powder and films have been obtained and computer analyzed. The tellurium films were deposited at room temperature and were thus crystalline. These runs were used to optimize sample parameters and spectrometer adjustments. The calibration constant was extrapolated from the outer lines of α -iron at 80°K (10.88 mm/sec) by assuming spectrometer linearity. The observed parameters (isomer shift and quadrupole splitting) agree with previously published data within experimental error ⁽³⁾.

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Details of the spectra, including the curve fitting and analysis procedure, will be presented in the next technical report.

Thus far, spectra of samples containing natural Te have been employed. The use of ^{125}Te enriched material will provide considerable improvement in signal to noise ratio of the spectra. A satisfactory method of preparing fairly thick film samples on beryllium or copper substrates has been developed. When this procedure has been optimized, spectra of Te films in both amorphous and crystalline states will be obtained and compared.

b) Source Preparation

Initially, considerable effort was expended attempting to obtain a satisfactory ^{125}Te in $\beta\text{-TeO}_3$ source for the Mossbauer experiments. This source has been reported ⁽⁴⁾ to give a single line of nearly natural width and a recoilless fraction $f = 0.58$ at 80°K, compared with a width of 1.4 times the natural width and a recoilless fraction $f = 0.26$ for the more commonly used ^{125}I in Cu. The commercial supplier (New England Nuclear Corp.) was unable to prepare stable $\beta\text{-TeO}_3$ according to the published prescriptions. Detailed information concerning the preparation technique for $\beta\text{-TeO}_3$ is being sought. The source now being used is the standard one for tellurium Mossbauer experiments: ^{125}I in Cu - which has a 60-day half life. This should be satisfactory for initial experiments. The $\beta\text{-TeO}_3$ source will be obtained when the supplier is able to meet the specifications.

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c) Specimen Preparation

Natural (unenriched) samples (e.g. TeO_3 , ZnTe and Te) were prepared by weighing out enough sample material to provide a areal density of 1.5 mg/cm^2 natural Te . The sample material was mixed with household granulated sugar to provide a homogeneous dispersal and the mixture was tightly encapsulated in a $5/8"$ dia. covered nylon dish. This method avoids the chemical decomposition associated with some high temperature encapsulation techniques and also eliminates the tendency of fine powders to coagulate when dispersed in epoxy or air drying cement.

Tellurium films were deposited by vacuum evaporation at approximately 10^{-5} Torr onto room temperature fused silica, beryllium foil or copper substrates. The thermal expansion coefficients of Te , Be and Cu are nearly equal, so that much thicker films can be deposited on Be or Cu than can be successfully deposited on the fused silica. The thickest film so far deposited appears to be unstrained and has been cycled between room temperature and 80°K without ill effect. This film is ~ 18 microns thick on a 10 mil Be substrate ($10.6 \text{ mg/cm}^2\text{Te}$). A large initial charge ($\sim 1\text{g}$) was used to prepare this film and the technique is being refined so as to use as small a charge of enriched material as possible in preparing the film. (Tellurium enriched to $\sim 80\%$ ^{125}Te costs nearly $\$1.00/\text{mg.}$)

C. FUTURE PLANS

Tellurium samples deposited on beryllium or copper foils and having the requisite ^{125}Te density ($\sim 1.5 \text{ mg/cm}^2$) will be

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prepared in the amorphous state by deposition on cold ($\sim 80^{\circ}\text{K}$) substrates. These will be kept cold during transfer to the Mossbauer spectrometer and spectra will be obtained. The same samples will be allowed to warm to room temperature, become crystallized and again analyzed by Mossbauer spectroscopy. The two sets of spectra will be computer analyzed for differences between them. The temperature and nature of the crystallization process will also be determined by means of resistivity measurements of films prepared identically to those used in the Mossbauer measurements. The apparatus and technique for doing this will be described in the next technical report.

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